

## LECTURE

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## Recent trends in solid mass spectrometry: GDMS and other methods

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**Abstract** An overview is given of three mass spectrometric techniques that can be applied for solid analysis: spark source mass spectrometry (SSMS), glow discharge mass spectrometry (GDMS) and inductively coupled plasma mass spectrometry (ICP-MS). Some benefits and limitations, and some typical applications of these techniques are discussed.

## 1 Introduction

A range of mass spectrometric techniques exists that can be employed for the trace analysis of solid materials. For bulk analysis of solids, glow discharge mass spectrometry (GDMS), spark source mass spectrometry (SSMS), and laser ionization mass spectrometry (LIMS) can be utilized, as well as inductively coupled plasma mass spectrometry (ICP-MS), either by dissolving the solid sample or by using an auxiliary (solid) sampling method. Surface analysis and depth profiling are possible with GDMS, whereas ICP-MS, in combination with a focused laser beam, can be used for microanalysis: laser microprobe (LAM)-ICP-MS. Other mass spectrometric techniques suitable for these purposes include secondary ion mass spectrometry (SIMS), sputtered neutrals mass spectrometry (SNMS), and laser assisted microprobe mass analysis (LAMMA). In the present review, only three of these techniques will be discussed, i.e., SSMS, ICP-MS, and GDMS, with the most attention being paid to the latter one.

## 2 Spark source mass spectrometry (SSMS)

SSMS is one of the oldest commercial forms of solids mass spectrometry [1]. It was especially popular in the

1960's and 1970's. Mass spectrometric separation is always realized in a double focusing instrument with Mattauch-Herzog geometry, and the ions of all masses ranging from Li to U, are simultaneously recorded on an ion-sensitive emulsion (photoplate). The photoplate is read out with a micro-densitometer, mostly under computer control. This equipment is, however, not produced anymore on a commercial basis, and some of the old instruments, constructed in the 1960's and 1970's, are being replaced in recent years by GDMS instruments. Nevertheless, SSMS is still used on a routine basis in several laboratories, and there are still some methodological developments. Jochum and coworkers developed a multi-ion counting (MIC) technique [2]; a detector array consisting of 20 separate channeltrons of 1.8 mm wide, allows simultaneous detection of 20 trace elements in 10–60 minutes. Compared to conventional SSMS using photoplate detection, this gives an improvement in sensitivity by more than a factor of 20. Satisfactory quantitative analysis can be performed: precisions are about 1–2% for concentrations of  $>0.1 \mu\text{g/g}$  and about 4% for concentrations in the order of  $0.01 \mu\text{g/g}$ . The mass range can be switched rapidly by changing the magnetic field. This method has been applied to the trace analysis of geological samples [2]. By isotopic spiking, isotope dilution can be carried out, with excellent precision and accuracy.

## 3 Glow discharge mass spectrometry (GDMS)

SSMS exhibits a high sensitivity, large applicability and in practice spectral interferences only from multiply charged ions, but it does not yield a stable ion population and hence requires an integrating detector. More recently, attention has been shifted gradually towards GDMS, because the glow discharge acts as a stable, low energy ion source. Description of the glow discharge (how it is created, the subdivision in different

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spatial regions, the species present in the plasma, and the occurrence of the different processes) can be found in other reviews [3–5]. For good analytical practice, a clear insight in the glow discharge processes is desirable. In our group, we try to achieve this by mathematical modeling, as is described, e.g., in [6–8]. Typical results of these models are the three-dimensional density profiles, fluxes and energy distributions of the different plasma species, the three-dimensional potential and electric field distribution, information about the collision processes in the plasma, crater profiles due to sputtering at the cathode, etc. Reasonable agreement with experiment has been reached, as is demonstrated in [9–11]. More details about this work can be found in the cited papers. In this review, we focus on the analytical applications of GDMS.

The most important applications of GDMS are found in the bulk analysis of metals. Due to the low detection limits of this technique for almost all elements of the periodic table, it is of particular interest for analyzing high-purity metals. For trace analysis, a high resolution instrument is particularly suitable, since many spectral interferences can then be eliminated. The only high resolution instruments that are commercially available are double focusing sector instruments, i.e., the “VG9000” (VG Elemental, Thermo instruments), the “Element” (Finnigan MAT), and the “Concept” (Kratos). For example, the analysis of high-purity aluminium (impurities of only a few ng/g) with the VG9000 instrument yields typical RSD values of 5% at concentration of about 1 µg/g and of 15–20% at concentrations in the order of 10 µg/g [12]. Due to surface contaminations (e.g., due to machining), it can take, however, some time (e.g. 20 min) before a stable intensity is reached. Surface segregation of certain elements as a result of liquid–solid transition was noticed in the analysis of high-purity gallium (melting point 29.78 °C) with the VG9000 GDMS system [13]. In the latter work, a comparison was made between GDMS (VG9000 instrument) and SSMS. It was found that, since GDMS sputters the sample layer by layer, and since the VG9000 instrument uses electrical sequential detection, heterogeneities in the sample are detected (depth profiling) and can give a false representation of the overall concentration, whereas the photoplate (simultaneous) detector in traditional SSMS can integrate the signal over time and can therefore average out heterogeneities, especially since the spark consumes much more material and samples the total diameter of the electrode. It appears that SSMS and GDMS are often complementary: SSMS offers a rapid survey of all elements present in the sample, and GDMS can analyze these elements with higher accuracy, if the material does not suffer from heterogeneities.

It is, in principle, also possible to obtain sub-µg/g detection limits with a quadrupole (i.e. low resolution) glow discharge mass spectrometer. This was demonstrated recently by Valiga et al. for the analysis of

a high purity gold sample, using an ultra-high purity discharge gas delivery system (consisting e.g., of a particle filter, a hot and a cold getter, cryocooling, etc.), so that most interfering peaks in the mass spectrum (except the ones ascribable directly to argon) have disappeared [14].

Beside high purity metals, also metallic alloys [15] and semiconductors [16] can be analyzed directly with GDMS. The analysis of nonconductors can, however, not directly be carried out with direct current (dc) GDMS. Indeed, the sample acts as cathode of the glow discharge, which is sputter-bombarded by positive ions, and nonconductive materials would hence be electrostatically charged up. Two modifications to overcome this problem are reported in the literature. The first exists in mixing the nonconductive sample as a powder with a conductive binder (Cu, Ag, Ga) and pressing it into an electrode [17, 18]. However, this mixing procedure results in an increase in sample preparation time compared to direct analysis of solids, it can introduce contaminations and leads to increased stabilization time of the discharge. The second approach is the use of a metallic secondary cathode diaphragm in front of the flat nonconductive sample surface. Due to the redeposition of a fraction of the sputtered metal atoms from the secondary cathode, a very thin conductive surface is formed on the nonconductive material, which allows atomization of the nonconductive sample as well. This method was first introduced by Milton and Hutton [19], and has recently been applied to the analysis of atmospheric particulate matter [20], ceramics [21], glass [22], polymers [23] and radionuclides in sediment samples [24].

Beside these two modifications in dc GDMS, also radio frequency (rf) powered GDMS can be employed for analyzing nonconductors directly, since the positive charge accumulated during one half-cycle will be neutralized by negative charge accumulation during the next half-cycle, so that no charging up occurs. Operation with rf power of a glow discharge using a nonconductive sample yields a negative dc bias voltage on the sample surface. Indeed, during the half-cycles in which the nonconductive electrode is positive, surface charging will occur much faster than in the half-cycles in which the electrode is negative, due to the much higher mobility of the electrons compared to the positive ions. This self-bias phenomenon permits to establish a time-averaged cathode and anode in the glow discharge, so that sputter-bombardment of positive ions on the cathode is possible. The ability to analyze nonconductors directly is one of the major advantages of rf-GDMS. Another advantage is that, since the electrons try to follow the rf electric field, they oscillate between the electrodes and give rise to a higher degree of ionization, so that rf discharges can be operated at lower pressures for the same current than dc discharges, resulting in less redeposition and spectral interferences. A large number of publications have appeared in the last years about

methodological developments and analytical applications of rf-GDMS [25–29]. Rf glow discharges have been combined with various types of mass spectrometers (quadrupole, Fourier transform, ion trap, time-of-flight and different sector-based instruments), but up to now, there is no commercial rf-GDMS available.

Apart from dc- and rf-GDMS, a third operation mode exists, i.e., the pulsed mode, which is gaining increasing importance in the last years [30–33]. Voltage and current are applied only during short periods of time (generally milliseconds), so that, compared to dc discharges, higher peak voltages and currents can be obtained for the same average power, yielding bombarding plasma species with higher energies, and hence more sputtering and a better analytical sensitivity. Moreover, it appears that the analytically important ions and the interfering ions are formed during different times in the pulse. Therefore, by coupling the time-dependent production of ions to a time-resolved detection, spectral interferences in the mass spectrum can be reduced. Recently, the microsecond pulsed discharge has been introduced, which yields still better analytical sensitivity, due to the still higher peak currents and voltages that can be applied during the short pulses [32, 33].

Another method to improve the performance of GDMS is the application of a magnet to the glow discharge, resulting in magnetron assisted discharges [34–36]. Permanent magnets are used to form a magnetic field of a few hundred Gauss in the plasma, so that electrons are forced to move in closed-loop trajectories parallel to the cathode surface. Hence, the electron path length is increased and the degree of ionization is significantly enhanced, so that the magnetron discharges can also operate at lower pressure than dc discharges for the same current. Lower pressure operation provides higher energies, leading to more sputtering and more ionization, and hence a better analytical sensitivity. However, the sputtering in a magnetron is more or less confined to a ring, yielding non-uniform crater shapes [36], which is unfavorable for depth profiling.

ICP-MS is a very popular, but an intrinsically solution based technique. However, there is considerable interest to adapt ICP-MS for the analysis of solid samples, to widen the application field. It is often possible to dissolve the solid sample to form solutions for aspiration into the plasma. However, this method has several disadvantages, i.e., contamination, the need for dilution, and it is time consuming. In many instances, it is desirable to analyze solid samples directly. Table 1 illustrates a number of solid sampling techniques, which have already been combined with ICP-MS, with their advantages and disadvantages.

With ETV-ICP-MS, a variety of sample types can be analyzed, but mostly after being dissolved prior to analysis. Direct solid analysis is, however, possible, as is demonstrated by Moens and coworkers, in the analysis of soil, sediments, fly ash, plant materials, etc. [37, 38]. Lüdke et al. used this technique for the analysis of atmospheric particulate matter [39]. The problematic of quantification is discussed in [40] by using the  $\text{Ar}_2^+$  signal as an internal standard.

LA-ICP-MS is gaining increasing importance in the last years and can be seen as a strong competition for (dc) GDMS, because it is able to analyze nonconductive materials directly. However, it is not straightforward to obtain really quantitative results with LA-ICP-MS. Depending on the laser spot diameter, LA-ICP-MS can be employed for micro-analysis (spot diameter of 1–100  $\mu\text{m}$ , sampled volume of 1–10<sup>6</sup>  $\mu\text{m}^3$ ) or for bulk analysis (spot diameter of 100  $\mu\text{m}$  to more than 1 mm, sampled volume of 0.0001 to >1 mm<sup>3</sup>). Watling et al. characterized the elemental “fingerprint” from gold samples with LA-ICP-MS, in order to associate these samples to a specific origin [41]. Gold and silver samples were also analyzed by Kogan and coworkers; an accuracy of better than 10% could be achieved for concentrations in the low  $\mu\text{g/g}$  range, using matrix matched standards [42]. Becker et al. measured “doped”  $\text{La}_{0.6}\text{Sr}_{0.35}\text{MnO}_3$  layers with

**Table 1** Overview of different solid sampling techniques in ICP-MS, with their specific features and drawbacks

| Technique                   | Features  | Drawbacks  |
|-----------------------------|---|--|
| Direct sample introduction  | *high sampling efficiency<br>*microsamples (powders)                      | *selective volatilization<br>*transient signals        |
| Slurry atomization          | *powders<br>*easy calibration   | *small particle size                                   |
| Electrothermal vaporization | *matrix separation →<br>reducing interferences                            |  |
| Laser ablation              | *conducting and<br>non-conducting samples<br>*spatial resolution possible | *sample must be<br>homogeneous for bulk<br>information |
| Spark ablation              | *low matrix effects<br>*high precision                                    | *sample must be conducting<br>and homogeneous          |

impurities at the  $\mu\text{g/g}$  level with LA-ICP-MS [43]. The results were in reasonable agreement with results of ICP-MS and of SSMS.

Whereas in the past infrared (IR) lasers were mainly used, which yielded crater diameters of 50  $\mu\text{m}$ , there is a tendency now to shift to ultraviolet (UV) lasers, to obtain smaller crater diameters (in the order of 10  $\mu\text{m}$ ), and to avoid melting of the sample. In [44] it was demonstrated that for many minerals laser ablation is more easily controlled using laser radiation in the UV than in the IR, and it provides higher spatial resolution (LAM-ICP-MS). Günther and coworkers could obtain detection limits of many elements in minerals at the  $\mu\text{g/g}$  level with LAM-ICP-MS, as is shown in [45].

## 5 Conclusion

The different mass spectrometric techniques that can be employed for solid analysis are often seen as competitors, but they should rather be considered as complementary techniques. SSMS is very suitable to yield a rapid overview of the general elemental composition of samples (i.e., which elements are present), and can easily be applied to non-conducting powders, by mixing them with, e.g., high-purity silver powder. GDMS can focus then on these elements, determine the analytical concentrations more exactly or at higher sensitivity (e.g., in high-purity metals), or detect sample heterogeneities (surface versus bulk). When comparing GDMS and ICP-MS, it seems that at the moment GDMS is still the only technique with sufficient sensitivity for directly analyzing ultra-pure (conductive) materials. However, the application field of ICP-MS, an intrinsically solution based technique, is being widened to the analysis of solids as well. The combination of one mass spectrometer, equipped with two sources, either for GDMS or for ICP-MS (with the possibility of laser ablation) opens the way to elemental analysis of almost all sample types, ranging from gases and liquids to conductive and nonconductive solids, and possibly combined with spatial information.

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